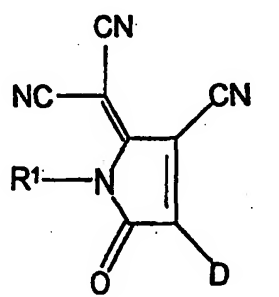
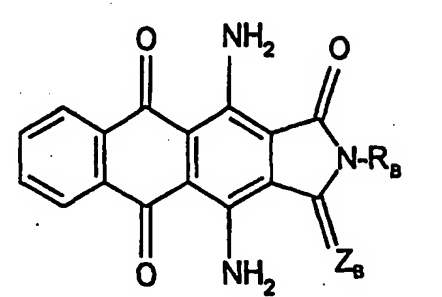


PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁷ : C09B 67/22, D06P 3/54</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/22048 (43) International Publication Date: 20 April 2000 (20.04.00)</p>
<p>(21) International Application Number: PCT/GB99/03300 (22) International Filing Date: 6 October 1999 (06.10.99) (30) Priority Data: 9822336.5 13 October 1998 (13.10.98) GB (71) Applicant (for all designated States except US): BASF AKTIENGESELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): LEAVER, Alan [GB/GB]; 12 Egerton Road, Eccles, Manchester M30 9LR (GB). BRIERLEY, David [GB/GB]; 3 Turfand Avenue, Royton, Oldham OL2 6EL (GB). BULLOCK, James, Franklin [GB/DE]; Strahlenberger Strasse 50, D-69198 Schriesheim (DE). (74) Agents: COLEIRO, Raymond et al.; Mewburn Ellis, York House, 23 Kingsway, London WC2B 6HP (GB).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: DISPERSE DYE MIXTURES</p> <p>(57) Abstract</p> <p>A dye mixture comprises: a) at least one pyrroline type dye of formula (I), wherein R¹ is H, C₁₋₂₀alkyl or C₂₋₂₀alkenyl; and D is aryl; and b) at least one anthraquinone type dye of formula (II), wherein R_B is (CH₂)_nOR_B¹; R_B¹ is C₁₋₆alkyl or C₁₋₆alkoxy-C₁₋₆alkyl; n is 1-6; and Z_B is O or NH.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>(I)</p> </div> <div style="text-align: center;">  <p>(II)</p> </div> </div>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

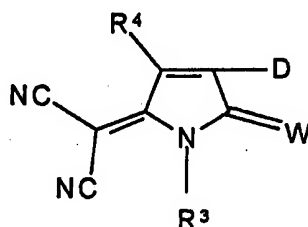
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

DISPERSE DYE MIXTURES

This invention relates to mixtures of disperse dyes, compositions comprising dispersions of such mixtures and processes for the colouration of synthetic materials with such mixtures. More particularly, the invention relates to mixtures of the dyes of the so-called pyrroline type with those of the so-called anthraquinone type.

Dyes of the pyrroline type are disclosed, for example, in US-A-3013013, US-A-3013018, GB-A-2191498, EP-A-0327077, EP-A-0511625 and WO-A-94010248.

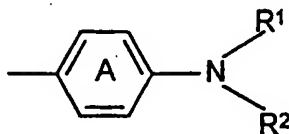
In particular, WO-A-94010248 discloses dyes of the pyrroline type having the formula (1)



Formula (1)

wherein:

D is a group of Formula (2):

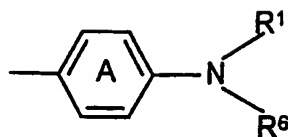


Formula (2)

2

or a group of Formula (3):

5

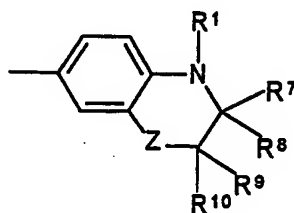


Formula (3)

10

or a group of Formula (4):

15



20

Formula 4

- R¹ is alkyl, cycloalkyl, aryl, alkenyl or aralkyl each of which may be optionally substituted;
- R² is optionally substituted C₇₋₂₀-alkyl; or
- 25 R¹ and R² together with the nitrogen atom to which they are attached form a pyrrolidino or piperidino ring;
- R³ is alkyl, alkenyl or aralkyl each of which may be optionally substituted, -SO₂alkyl, -SO₂aryl, or -COR in which R is -H or alkyl, phenyl, cycloalkyl or aralkyl each of which may be optionally substituted, or -H; and
- 30 R⁴ is an electron withdrawing group;
- R⁶ is optionally substituted C₁₋₁₆-alkyl; or
- 35 R¹ and R⁶ together with the nitrogen atom to which they

are attached form a pyrrolidino or piperidino ring;

R^7 , R^8 , R^9 and R^{10} each independently is alkyl, cycloalkyl, aryl, alkenyl or aralkyl, each of which may
5 be optionally substituted or -H;

W is oxygen or sulphur;

Z is a direct link or $N-R^{11}$ in which R^{11} is -H or optionally substituted alkyl or aryl;

Ring A is unsubstituted apart from the $-NR^1R^2$ group
10 or is substituted by from 1 to 4 further groups; and

Ring B is unsubstituted or substituted by from 1 to 3 groups; except for 3-(4-(N,N-di-n-octylamino)phenyl)-4-cyano-5-dicyanomethylidene-2-oxo-2,5-dihydropyrrole
15 provided that:

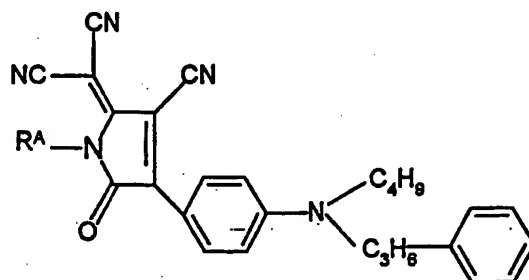
(a) when D is a group of Formula (3), R^1 and R^6 are different and R^1 is not $-C_2H_5$, $-C_3H_7$ or $-C_4H_9$ when R^6 is $-C_2H_4$ phenyl, $-C_3H_6$ phenyl and ethyl substituted by -OH,
20 -CN, $-OCH_3$, $-OC_2H_4OC_2H_5$, $-NHCOCH_3$, -Ophenyl and $-NHSO_2CH_3$;
or

(b) at least one of R^1 and R^6 is branched chain alkyl.

Commercially available dyes of the pyrroline type are, for example, dyes of the formula:

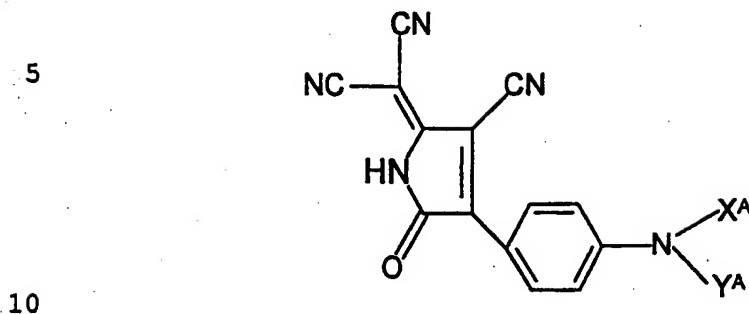
25

30



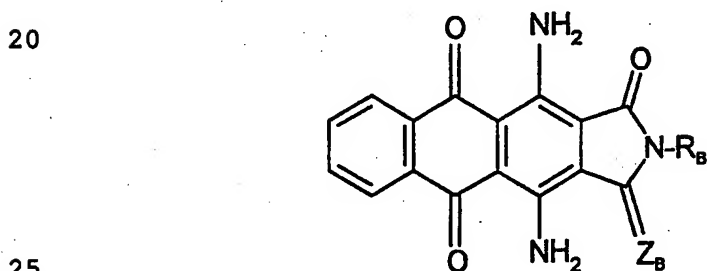
35 where R^A is H (Kayalon Polyester Brilliant Blue F2B-S);
or $CH_2CH=CH_2$ (Kayalon Polyester Blue-Green FG-S); and

dyes of the formula



where X^A is C_4H_9 , and Y^A is $CH(CH_3)C_5H_{11}$.

15 Dyes of the anthraquinone type are also well known. For example, dyes and mixtures of dyes each within the formula given below are commercially available as C.I. Disperse Blue 60 type dyes:



where R_B is $(CH_2)_n - O - R_B^1$, in which n is 1-6 and R_B^1 is straight or branched alkyl or alkoxy (and examples of R_B are $C_2H_5OCH_3$, $C_3H_7OCH_3$, $C_3H_7OC_2H_5$ and $C_3H_7OC_2H_4OCH_3$) and Z_B is O or NH.

30

However, if dyes of the pyrroline type alone (or mixtures of such pyrroline-type dyes) are dyed on polyester, build up to heavy depths of shade is difficult to achieve, light fastness is average at

35

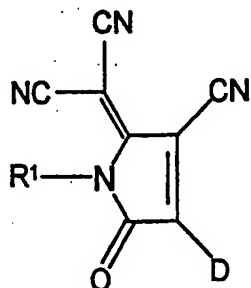
best, the dyes tend to be rather sensitive to changes in the pH of dyeing and undesirable redder shades are sometimes seen.

5 If dyes of the anthraquinone type alone (or mixtures of such anthraquinone-type dyes) are dyed on polyester, they often exhibit very good light fastness, but with poor build up. Moreover, they are tinctorially very weak and therefore expensive for colouring
10 polyester. Moreover, high strength liquid or grain formulations cannot be achieved. In addition, although good build up can be achieved, the shade becomes duller as the dye builds up.

15 We have now found surprisingly that if certain dyes of the pyrroline type are mixed with certain dyes of the anthraquinone type, brighter shades are maintained as the dyes build up. Moreover, the dyeings have good light fastness. In particular, as compared
20 with anthraquinone dyes alone, when using mixtures with pyrroline dyes, products of high colour strength can be readily formulated, with greater cost-effectiveness.

Thus the invention provides a dye mixture
25 comprising

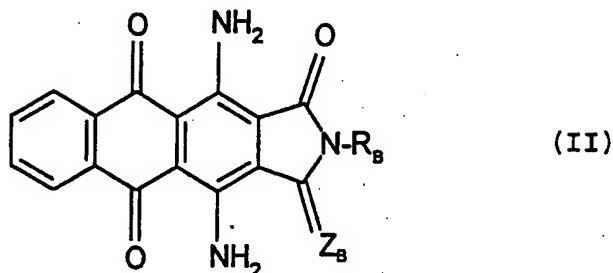
(A) at least one pyrroline type dye of the formula (I);



(I)

wherein R^1 is H, C_{1-20} alkyl or C_{2-20} alkenyl; and D is aryl; and

(B) at least one anthraquinone type dye of the formula (II)



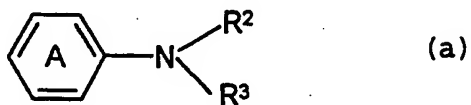
wherein R_B is $(CH_2)_nOR_B^1$;

R_B^1 is a straight or branched chain C_{1-6} alkyl or C_{1-6} alkoxy- C_{1-6} alkyl;

n is 1-6; and

Z_B is O or NH.

Component (A) preferably comprises a dye of the formula (I) wherein D is a group of the formula (a)



wherein each of R^2 and R^3 independently is an alkyl, cycloalkyl, aryl, alkenyl or aralkyl group.

In the above formula (I), the alkyl group represented by any of $R^1 - R^3$ is preferably a C_{1-20} -alkyl, more preferably a C_{1-12} -alkyl and especially a C_{1-8} -alkyl group. The cycloalkyl group represented by

R² or R³ is preferably a C₄₋₈-cycloalkyl and more preferably a cyclohexyl group. The aryl group represented by R² or R³ is preferably phenyl. The alkenyl group represented by any of R¹ - R³ is preferably a C₂₋₁₀-alkenyl, more preferably a C₂₋₆-alkenyl and especially a C₂₋₃-alkenyl group, such as allyl. The aralkyl group represented by any of R¹ - R³ is preferably a phenyl-C₁₋₆-alkyl, more preferably a phenyl-C₁₋₃-alkyl, especially phenylethyl or 3-phenylpropyl.

The alkyl group represented by R³ is more preferably a C₇₋₁₅-alkyl, still more preferably a C₇₋₁₂-alkyl and especially a C₇₋₉-alkyl group.

15

The alkyl group represented by R¹ is more preferably a C₁₋₆-alkyl and still more preferably C₁₋₄-alkyl group.

20

R¹ is especially preferably -H, C₁₋₄-alkyl or C₂₋₃-alkenyl, more preferably -H or C₁₋₄-alkyl and especially -H.

D is preferably a group of Formula (a).

25

The alkyl groups represented by any of R¹ - R³ may be straight or branched chain alkyl groups. R² is preferably C₁₋₁₂-alkyl more preferably C₁₋₈-alkyl especially unsubstituted C₁₋₈-alkyl. R³ may be C₇₋₁₂-alkyl and preferably C₇₋₉-alkyl, especially unsubstituted C₇₋₉-alkyl or may be unsubstituted C₁₋₆-alkyl. Where D is a group of Formula (a) it is preferred that one or both of R² and R³ is branched, more preferably branched at an α - or β -, i.e. 1- or 2-, position. It is preferred that R² and R³ are different. It is also preferred that ring A is unsubstituted apart from the

35

NR²R³ group.

A preferred sub-group of dyes of Formula (I) is that in which D is a group of Formula (a):

- 5 R¹ is alkyl or -H;
 R² is alkyl;
 R³ is C₇₋₂₀-alkyl; and
 Ring A is unsubstituted apart from the -NR²R³ group.

- 10 Another preferred sub-group of dyes of Formula (I) is that in which D is a group of the Formula (a);

- R¹ is -H or alkyl;
 R² is unsubstituted C₁₋₈-alkyl;
 R³ is unsubstituted C₁₋₆-alkyl; and
15 Ring A is unsubstituted apart from the -NR²R³ group; and
 R² and R³ are different or at least one of R² and R³ is a branched chain alkyl.

- 20 An especially preferred sub-group of dyes of Formula (I) is that in which D is a group of Formula (a):

- R¹ is -H;
 R² is unsubstituted C₁₋₈ alkyl;
25 R³ is unsubstituted C₇₋₉ alkyl; and
 Ring A is unsubstituted apart from the -NR²R³ group.

- 30 A further especially preferred sub-group of dyes of Formula (I) is that in which D is a group of Formula (a);

- R¹ is -H;
 R² is n-propyl or n-butyl;
35 R³ is 1-methylhexyl or 2-ethylhexyl; and

Ring A is unsubstituted apart from the $-NR^2R^3$ group.

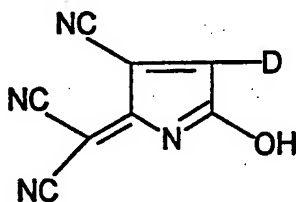
Typical especially preferred components (A) in mixtures embodying the invention are:

5 (1) a pyrroline type dye of the formula (I), wherein R^1 is H, R^2 is C_4H_9 , and R^3 is 1-methyl-n-hexyl (A^1) or a mixture thereof with up to 10% by weight of component (A), of a pyrroline type dye (A^2) of the formula (I), wherein R^1 is H and each of R^2 and R^3 is
10 C_4H_9 ;

(2) a pyrroline type dye of the formula (I), wherein R^1 is H, R^2 is ethyl and R^3 is n-octyl (A^3) or 2-ethyl-n-hexyl (A^4) or a mixture of dyes (A^3) and (A^4); and

15 (3) a pyrroline type dye of the formula (I), wherein R^2 is C_4H_9 , R^3 is 3-phenylpropyl and R^1 is H (A^5) or allyl (A^6) or a mixture of dyes (A^5) and (A^6).

When R^1 is H, dyes of Formula (I) may exist in a
20 tautomeric form represented by Formula (IA):



Formula (IA)

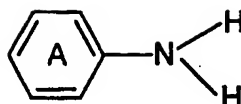
30

wherein:

D is as hereinbefore defined.

The dyes of Formula (I) where D is a group of Formula (a) may be prepared by reaction of an aniline
35 of Formula (III):

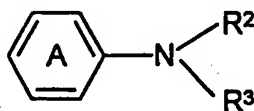
5



Formula (III)

10 in which Ring A is as hereinbefore defined, firstly
with a compound of Formula R^2X in which R^2 is as
hereinbefore defined and X is a halogen such as -Cl,
-Br or -I or other leaving group, such as a tosylate,
mesylate or alkylsulphonate in the presence of a base
15 such as an alkali metal carbonate or alkaline earth
metal carbonate such as K_2CO_3 or $CaCO_3$ and secondly with
a compound of formula, R^3X in which R^3 and X are as
hereinbefore defined in the presence of a base as above
to form an aromatic amine of Formula (IV);

20



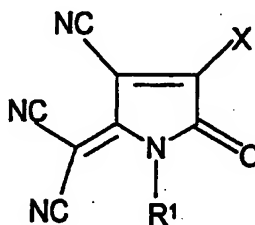
25

Formula (IV)

Alternatively the aromatic amine of the Formula (IV)
may be prepared by reductive alkylation of the aniline
30 of Formula (III) with an appropriate ketone or
aldehyde. The reductive alkylation may be performed in
an inert liquid medium such as an alcohol or ester
optionally in the presence of an acid such as an
aliphatic carboxylic acid, for example, acetic and
35 propionic acids and aromatic sulphonic acid e.g. 4-

toluenesulphonic acid using a metal or supported metal catalyst such as palladium or platinum on carbon and hydrogen, optionally at elevated temperature and pressure. Alternatively, reducing agents such as sodium borohydride may be used. After the reductive alkylation a second alkyl group may be introduced as described above.

The aromatic amine of Formula (IV) is then reacted with a 3-halopyrrole of Formula (V):

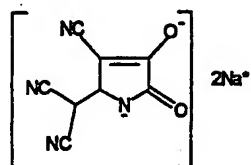


Formula (V)

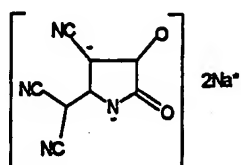
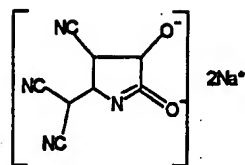
in which R¹ is as hereinbefore defined and X is preferably a halogen such as -Cl or -Br to form a compound of Formula (I). The reaction may be performed in a liquid medium such as N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulphoxide, sulfolane, N-methylpyrrolidone, acetonitrile, toluene or tetrahydrofuran or any mixture thereof and at a temperature from -20°C to 50°C. The product may be isolated by any convenient means such as pouring the reaction mixture into a mixture of ice and water and recovering the precipitated product by filtration. The product may be purified by any convenient means such as trituration or recrystallisation from organic liquids particularly alkanols such as methanol, ethanol and esters such as ethylacetate or mixtures thereof.

The 3-halo-2-oxopyrrole of Formula (V) may be

prepared by halogenation of a compound which may be represented by Formulae (VI), (VI¹) and (VI²)



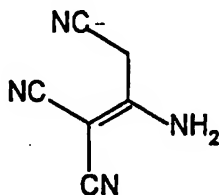
Formula (VI)

Formula (VI¹)Formula (VI²)

5 with a halogenating agent such as phosphorus oxychloride, phosphorus trichloride, phosphorus pentachloride, thionyl chloride or phosgene at a temperature of from -20°C to 50°C in a liquid medium such as N,N-dimethylformamide, N,N-diethylacetamide, 10 dimethylsulphoxide, sulpholane, N-methylpyrrolidone, acetonitrile or tetrahydrofuran. The product may be used without isolation with improvement in yield in the preparation of compounds of Formula (1) described above or may be isolated by evaporating the liquid medium.

15 Alternatively a compound of Formula (IV) may be reacted directly with the compound represented by Formulae (VI), (VI¹) or (VI²) in a liquid medium such as toluene in the presence of a halogenating agent such as phosphorus oxychloride.

20 The compounds represented by Formulae (VI) or (VI¹) may be prepared by reaction of diethyloxalate with a compound for Formula (VII);



Formula (VII)

in the presence of a base such as an alkali metal alkoxide preferably a sodium or potassium C₁₋₆-alkoxide and especially sodium or potassium methoxide, ethoxide, n- or iso-propoxide, n-, iso- or tertiary-butoxide in a liquid medium, preferably an alkanol such as methanol, ethanol, n- or iso-propanol or n-, iso- or tertiary-butanol, at a temperature of from 10°C to 60°C. The product may be isolated by cooling the reaction mixture and collection by filtration.

10 The compound of Formula (VII) may be prepared by reaction of malononitrile with a compound of Formula (VIII):

[illegible]

in the presence of a base such as sodium methoxide in a liquid medium such as methanol at a temperature of from -20°C to 60°C. The product may be isolated by filtration.

A dye of Formula (I) in which R¹ is other than -H may be prepared by reaction of the corresponding dye of Formula (I) in which R¹ is -H in a liquid medium, preferably an amide such as dimethylformamide or an ether such as tetrahydrofuran or diethylether in the presence of a base, preferably an alkali metal carbonate such as potassium carbonate or an alkali metal hydride such as sodium hydride at a temperature of 0°C to 120°C with an appropriate alkylating agent. Where R¹ is alkyl an appropriate alkylating agent is an alkyl halide, preferably an alkyl iodide, bromide or chloride. Where R¹ is alkenyl an appropriate alkylating agent is an alkenyl halide, preferably an alkenyl bromide. These dyes may be isolated by

evaporating the liquid medium or by filtration from the reaction mixture.

As previously mentioned, component (A) may be a mixture of two or more dyes of Formula (I) wherein R^1 to R^3 inclusive, D and Ring A are as hereinbefore defined.

Reference is now made to component (B), which preferably comprises at least one anthraquinone type dye of the formula (II), wherein Z_b is O or NH, more preferably O, n is 1, 2 or 3, more preferably 2 or 3 and R_b^1 is methyl, ethyl or methoxyethyl. Thus, it is especially preferred that component (B) is an anthraquinone dye of the formula (II) wherein Z_b is O and R_b is $C_2H_4OCH_3$, $C_3H_6OCH_3$, $C_3H_6OC_2H_5$ or $C_3H_6OC_2H_4OCH_3$ or a mixture of any two or more such anthraquinone type dyes, especially a mixture of any two, or all three, of the dyes (B^1), (B^2) and (B^3), each of the Formula (II) in which Z_b is O,

which dye (B^1) is a dye wherein R_b is $C_3H_6OCH_3$,
which dye (B^2) is a dye wherein R_b is $C_3H_6OC_2H_4OCH_3$;
and

which dye (B^3) is a dye wherein R_b is $C_3H_6OC_2H_5$.

When component (B) is a mixture of dyes (B^1) and (B^2), the ratio by weight of dye (B^1) : dye (B^2) is preferably from 30:70 to 60:90 inclusive, more preferably from 45:55 to 48:52.

The dyes of the formula (II) wherein R_b is hydrogen may be prepared, for example, by reaction of 2,3-dicyano-1,4-diamino-anthraquinone with sulphuric acid. This dye may then be reacted with a primary amine $R_b^xNH_2$ to obtain a dye of the formula (II) wherein R_b^x is any of the groups of R_b other than hydrogen. Alternatively, certain of such dyes of the formula (II) may be prepared from the 2,3-dicyano-1,4-

diaminoanthraquinone by reaction with each of sulphuric acid and a secondary alcohol to provide a dye wherein R_b^x is secondary alkyl. Another method of preparing dyes of the formula (II) where R_b is a group as previously defined other than hydrogen is by reaction of the corresponding 1,4-diaminoanthraquinone carboxylic anhydride with a primary amine $R_b^xNH_2$ where R_b^x is as defined above. Such reactions are disclosed in Ventkataraman, The Chemistry of Synthetic Dyes, Academic Press, New York and London, 1970, Vol. III, pages 413-415.

In general, in a preferred mixture of components (A) and (B), the ratio by weight, of component (A): component (B) is from 3:97 to 60:40 inclusive, more preferably from 8:92 to 40 : 60 inclusive, especially from 10:90 to 30:70 inclusive.

In especially preferred mixtures of components (A) and (B), component (A) is

(1) a pyrroline type dye of the formula (I), wherein R^1 is H, R^2 is C_4H_9 , and R^3 is 1-methyl-n-hexyl (A^1) or a mixture thereof with up to 10% by weight of component (A), of a pyrroline type dye (A^2) of the formula (I), wherein R^1 is H and each of R^2 and R^3 is C_4H_9 ; or

(2) a pyrroline type dye of the formula (I), wherein R^1 is H, R^2 is ethyl and R^3 is n-octyl (A^3) or 2-ethyl-n-hexyl (A^4) or a mixture of dyes (A^3) and (A^4); or

(3) a pyrroline type dye of the formula (I), wherein R^2 is C_4H_9 , R^3 is 3-phenylpropyl and R^1 is H (A^5) or allyl (A^6) or a mixture of dyes (A^5) and (A^6); and

component (B) is a mixture of anthraquinone-type dyes (B^1) and (B^2), each of the formula (II), which dye (B^1) is a dye wherein Z_b is O and R_b is $C_3H_7OCH_3$, and which dye (B^2) is a dye wherein Z_b is O and R_b is

$C_3H_5OCH_2CH_2OCH_3$, wherein the ratio, by weight, of the dye (B¹) : dye (B²) is preferably from 45 : 55 to 48 : 52.

At least for a mixture of component A(1), with component (B), the ratio, by weight, of component A(1) : component (B) is preferably from 5 : 90 to 30 : 70 inclusive.

A mixture embodying the invention of at least one dye of formula (I) (component A) and at least one dye of the formula (II) (component B) may additionally comprise at least one other dye (component C), especially a yellow, orange, red or brown dye capable of producing a navy or black shade.

Mixtures embodying the invention can be prepared by a number of methods including

(1) Co-crystallisation

Typically, the dyes are dissolved in a hot solvent, for example, by placing the dyes in a suitable solvent and heating up to the reflux temperature of the solvent until the dyes are dissolved, thereafter filtering to provide a solution, and then allowing the solution to cool and crystals to form. The resultant mixture may then undergo further processing, such as milling and spray drying. Examples of suitable solvents for this process are organic solvents such as aromatic hydrocarbons, chlorinated hydrocarbons, aliphatic hydrocarbons, alicyclic hydrocarbons, alcohols, amides, sulphoxides, esters, ketones and ethers. Specific examples of organic solvents are toluene, ethyl cellosolve, acetone, chlorobenzene, pyridine, dimethyl formamide, diethylsulphoxide, ethyl acetate, benzene, tetrahydrofuran and cyclohexane.

(2) Co-milling

(a) The dyes are mixed and then milled together to give an intimate blend which is then spray dried to
5 give a solid mixture; or

(b) each dye is milled separately and then mixed in the required ratio before spray drying.

(3) Dry Blending

10 Each dye is spray dried separately and then mixed in the required ratio by a dry blending process.

The mixtures give especially bright shades which
15 are maintained as the dyes build up. Dyeings with the mixtures have good light fastness. The mixtures have high colour strength and can be readily and cost-effectively formulated.

20 Mixtures embodying the invention provide especially useful disperse dyes valuable for colouring synthetic textile materials and fiber blends thereof by exhaust dyeing, padding or printing, and may be formed into dispersions for this purpose. They may also be
25 used in, for example, ink jet printing of textiles and non-textiles, dye diffusion, thermal transfer printing and in the colouration of plastics.

According to other aspects, the invention provides a composition comprising at least the dye mixture and a
30 dispersing agent, surfactant or wetting agent, suitable for providing such a dispersion and also a process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material or fibre blend a mixture comprising at
35 least one dye of the formula (I) and at least one dye of the formula (II).

The synthetic textile material may be selected from aromatic polyester, especially polyethylene terephthalate, polyamide, especially polyhexamethylene adipamide, secondary cellulose acetate, cellulose triacetate, and natural textile materials, especially cellulosic materials and wool. An especially preferred textile material is an aromatic polyester or fibre blend thereof with fibres of any of the above mentioned textile materials. Especially preferred fibre blends include those of polyester-cellulose, such as polyester-cotton, and polyester-wool. The textile materials or blends thereof may be in the form of filaments, loose fibres, yarn or woven or knitted fabrics.

The mixtures of dyes of formulae [I] and [II] optionally in conjunction with other disperse dyes may be applied to the synthetic textile materials or fibre blends by processes which are conventionally employed in applying disperse dyes to such materials and fibre blends.

Suitable process conditions may be selected from the following

- (i) exhaust dyeing at a pH of from 4 to 6.5, at a temperature of from 125°C to 140°C for from 10 to 120 minutes and under a pressure of from 1 to 2 bar, a sequestrant optionally being added;
- (ii) continuous dyeing at a pH of from 4 to 6.5, at a temperature of from 190°C to 225°C for from 15 seconds to 5 minutes, a migration inhibitor optionally being added;
- (iii) direct printing at a pH of from 4 to 6.5, at

- 5 a temperature of from 160°C to 185°C for from
4 to 15 minutes for high temperature
steaming, or at a temperature of from 190°C to
225°C for from 15 seconds to 5 minutes for
bake fixation with dry heat or at a
temperature of from 120°C to 140°C and 1 to 2
bar for from 10 to 45 minutes for pressure
steaming, wetting agents and thickeners (such
as alginates) of from 5 to 100% by weight of
the dye optionally being added;
- 10 (iv) discharge printing (by padding the dye on to
the textile material, drying and
overprinting) at a pH of from 4 to 6.5,
migration inhibitors and thickeners
optionally being added;
- 15 (v) carrier dyeing at a pH of from 4 to 6.5, at a
temperature of from 95°C to 100°C using a
carrier such as methylnaphthalene,
diphenylamine or 2-phenylphenol, sequestrants
optionally being added; and
- 20 (vi) atmospheric dyeing of acetate, triacetate and
nylon at a pH of from 4 to 6.5, at a
temperature of 85°C for acetate or at a
temperature of 90°C for triacetate and nylon
for from 15 to 90 minutes, sequestrants
optionally being added.
- 25

In all the above processes, the dye mixture may be
applied as a dispersion comprising from 0.001% to 6,
30 preferably from 0.005 to 4%, of the dye mixture in an
aqueous medium.

A particular aspect of the invention provides a
composition comprising a mixture of dyes (I) and (II),
optionally at least one other disperse dye and,
35 additionally, optionally at least one further

ingredient conventionally used in colouring applications such as a dispersing agent, surfactant or wetting agent. The composition typically comprises from 1% to 65%, preferably 10 to 60%, more preferably 20 to 55%, of the total dye mixture in a liquid, preferably an aqueous, or solid medium. Liquid compositions are preferably adjusted to pH 2 to 7, more preferably pH 4 to 6.

Typical examples of dispersing agent are lignosulphonates, naphthalene sulphonic acid/formaldehyde condensates and phenol/cresol/sulphanilic acid/formaldehyde condensates, typical examples of wetting agent are alkyl aryl ethoxylates which may be sulphonated or phosphated and typical examples of other ingredients which may be present are inorganic salts, de-foamers such as mineral oil or nonanol, organic liquids and buffers. Dispersing agents may be present at from 10% to 200% on the weight of the dye mixtures. Wetting agents may be used at from 0% to 20% on the weight of the dye mixtures.

The compositions may be prepared by bead milling the dye mixture with glass beads or sand in an aqueous medium. The compositions may have further additions of dispersing agents, fillers and other surfacants and may be dried, by a technique such as spray drying, to give a solid composition comprising from 5% to 65% of dyestuff.

In addition to the above-mentioned application processes, the dye mixtures may be applied to synthetic textile materials and fibre blends by ink-jet printing, the substrates optionally having been pre-treated to aid printing. For ink-jet applications, the application medium may comprise water and a water-soluble organic solvent, preferably in a weight ratio

of 1:99 to 99:1, more preferably 1:95 to 50:50 and especially in the range 10:90 to 40:60. The water-soluble organic solvent preferably comprises a C₁-C₄-alkanol, especially methanol or ethanol, a ketone, especially acetone or methyl ethyl ketone, 2-pyrrolidone or N-methylpyrrolidone, a glycol, especially ethylene glycol, propylene glycol, trimethylene glycol, butane-2,3-diol, thiodiglycol or diethylene glycol, a glycol ether, especially ethylene glycol monomethyl ether, propylene glycol monomethyl ether or diethylene glycol monomethyl ether, urea, a sulphone, especially bis-(2-hydroxyethyl) sulphone or mixtures thereof.

The dye mixtures may also be applied to textile materials using supercritical carbon dioxide, in which case the dye formulating agents may optionally be omitted.

Embodiments of the present invention will now be described in more detail with reference to the following Examples, in which parts are by weight unless otherwise stated.

Examples 1-2 Preparation for Individual Dyes

Example 1 - Pyrroline-type Dye (1)

Preparation of 3-(4-(N-butyl-N-(1-methylhexyl)amino)phenyl)-4-cyano-5-dicyanomethylidene-2-oxo-2,5-dihydropyrrole

i) A mixture of aniline (100 parts), 2-heptanone (220 parts), 4-toluene sulphonic acid (6 parts) and 3% palladium on carbon (5 parts) in a 1 litre autoclave was charged with hydrogen to a pressure of 80 atmospheres and heated at 150°C for 40 hours. The cooled reaction mixture was diluted with ethyl acetate, filtered, washed with 1N-hydrochloric acid (6 x 200

parts) and water (2x200 parts), the ethyl acetate was separated and dried (MgSO_4) before evaporating to leave N-(1-methylhexyl)aniline (76 parts, 37%).

ia) In an alternative procedure, N-(1-methylhexyl)aniline was prepared as follows: To an ice cooled, stirred mixture of aniline (28 parts), heptan-2-one (69 parts) and propionic acid (9 parts) was added sodium borohydride (9.8 parts) portionwise at such a rate as to keep the temperature less than 5°C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was then poured into an ice water mixture, and extracted with ethyl acetate. The organic phase was washed with water, 2% hydrochloric acid and water. The dried organic phase was evaporated to leave N-(1-methylhexyl)aniline (53.5 parts, 93%).

ii) A mixture of N-(1-methylhexyl)aniline (76 parts), 1-bromobutane (66 parts), anhydrous potassium carbonate (65 parts) and DMF (150 parts) was stirred while heating under reflux for 41 hours. An additional quantity of 1-bromo butane (44 parts) was added and the mixture stirred while heating under reflux for a further 19 hours. The cooled mixture was poured into water (400 parts) and the organic phase separated. The aqueous phase was extracted with toluene, the organic phases and toluene extract were combined and washed with water (2 x 100 parts) before evaporating to leave N-butyl-N-(1-methylhexyl)aniline (72.8 parts, 44%) which was purified by vacuum distillation to give N-butyl-N-(1-methylhexyl)aniline b.pt 73-80°C, 2.6 mm Hg. [Dye (1)].

iaa) In an alternative procedure, N-butyl-N-(1-methylhexyl)aniline was prepared as follows:

A mixture of N-butylaniline (7.45 parts) anhydrous potassium carbonate (7.5 parts), 2-bromoheptane (13.5

parts) and DMF (25 parts) was stirred at 130°C for 86 hours. The reaction mixture was poured into water, saturated with salt and extracted with ethyl acetate. The organic phase was washed with water, dried (MgSO₄) and evaporated to leave N-butyl-N-(1-methylhexyl)aniline (11.8 parts, approximately 60% strength). This material had acetic anhydride (10 parts) added to it prior to further use.

5 iii) A stirred mixture of the disodium salt of 4-cyano-5-dicyanomethylidene-3-hydroxy-2-oxo-2,5-dihydropyrrole (23 parts) and dry N,N-dimethylformamide (180 parts) was cooled to -5°C to -10°C and N-n-butyl-N-(1-methylhexyl)aniline containing acetic anhydride (27%, 37 parts) was added followed by the dropwise addition

10 of phosphorous oxychloride (26 parts) whilst maintaining the temperature at less than -5°C. The mixture was allowed to warm to room temperature and stirred for 20 hours. The reaction mixture was poured into a stirred mixture of ice and water (400 parts) and

15 acetone (400 parts) was added before filtering off a solid. The solid was washed repeatedly with warm water (40°C) and then dried at 50°C to yield 3-(4-(N-butyl-N-(1-methylhexyl)amino)phenyl)-4-cyano-5-dicyanomethylidene-2-oxo-2,5-dihydropyrrole (26.8

20 parts, 65%). A small sample of this material was slurried in boiling methanol, collected by filtration, washed with methanol and dried at 50°C to give 3-(4-(N-n-butyl-N-(1-methylhexyl)amino)phenyl)-4-cyano-5-dicyanomethylidene-2-oxo-2,5-dihydropyrrole m.p.

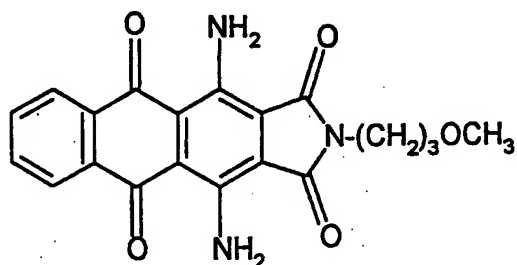
25 180°C; λ_{max} (CH₂Cl₂) 662nm (ϵ max 60231); M/Z (EI) 415 (M⁺, 20%), 400 (15), 372 (12), 344 (100), 288 (33) and 272 (25).

30

Example 2 - Anthraquinone-type Dye (2)

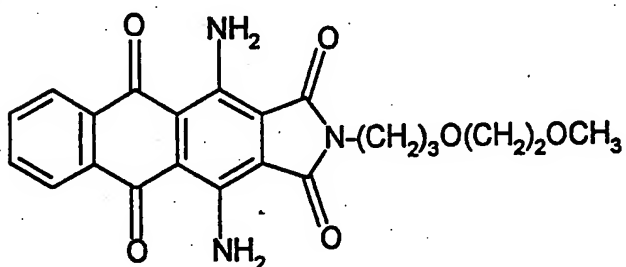
A dye (2) obtained commercially as C.I. Disperse Blue 60, is a mixture of 13.5 parts by weight Palanil Blue BG-ME and 25 parts by weight Palanil Blue BG-M, which mixture is made up to 100 parts by weight with dispersing agents. The dyes have the following respective structures.

10



Palanil Brilliant Blue BG-M

15



20

Palanil Brilliant Blue BG-ME

Examples 3-4 -Preparation of MixturesExample 3

5 A dye (1), synthesized as described in Example 1,
contained less than 10% by weight of the corresponding
N,N-dibutyl compound as impurity. A press paste of
this dye is bead milled as a 40% aqueous slurry with 20
parts of a high temperature stable dispersing agent
10 until the dye particle size (mean diameter) is in the
range of 0.1 - 5 microns.

A dye (2), as described in Example 2, is made up into a
press paste, which is also bead milled in the same
15 manner as a dye (1).

Each of the milled pastes of dyes (1) and (2) are
combined with one another and the dispersion was
standardized to a liquid brand containing 20.5% of the
20 mixture, by the addition of 6.5 parts of a humectant
and water (to 100 parts). This is especially suitable
for use in the direct printing and continuous dyeing of
polyester and polyester/cellulose blends and can also
be used for exhaust dyeing.

25 The same dispersion is standardised to a solid brand,
containing 12 parts of dye (1), 29 parts of dye (2) and
59 parts of dispersing agent, by the addition of 39
parts of a temperature stable dispersing agent and
30 drying to either a grain or powder form in a spray
dryer. The product is especially suitable for the
exhaust dyeing of polyester, polyester/cellulose and
polyester/wool blends and can also be used for
continuous dyeing and direct printing.

Example 4

Example 3 is repeated except that 100 parts of the
5 spray dried grains contain 6 parts of dye(1) and 33
parts of dye (2).

Examples 5-6

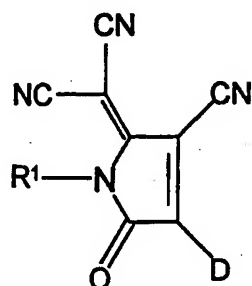
10

A dyebath for the exhaust dyeing of polyester in piece
form is prepared by adding 3mls of an aqueous
dispersion of the solid composition of Examples 3 and 4
respectively (1g dye in 100 ml water at 40-50°C) to
15 55.8ml of de-ionised water and 1.2ml of buffer
solution. To this dyebath is added a 5g piece of
polyester and the whole is held for 45 minutes at 130°C
in a Werner Mathis Labomat high temperature dyeing
machine. After rinsing with water and a reduction
20 clearing treatment, the material is dyed a bright
greenish-blue shade with excellent build up and light
fastness.

CLAIMS:

1. A dye mixture comprising

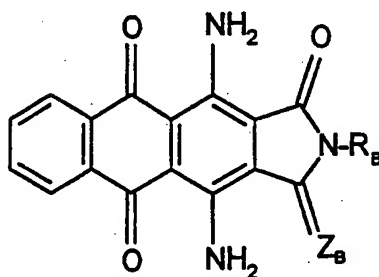
(A) at least one pyrroline type dye of the formula (I)



(I)

wherein R¹ is H, C₁₋₂₀alkyl or C₂₋₂₀alkenyl; and
D is aryl; and

(B) at least one anthraquinone type dye of the formula
(II)



(II)

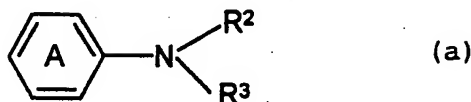
wherein R₈ is (CH₂)_nOR_B¹;

R_B¹ is C₁₋₆alkyl or C₁₋₆alkoxy-C₁₋₆alkyl;

n is 1-6; and

Z_B is O or NH

2. A dye mixture according to claim 1, wherein, in a dye of the formula (I) of the mixture, D is a group of the formula (a)



10 wherein each of R^2 and R^3 independently is an alkyl, cycloalkyl, aryl, alkenyl or aralkyl group.

15 3. A dye mixture according to claim 2, wherein D is a group of the formula (a), R^2 is as defined in claim 2 and R^3 is C_{7-20} alkyl.

20 4. A dye mixture according to claim 3, wherein R^2 is C_4H_9 and R^3 is 1-methyl-n-hexyl.

25 5. A dye mixture according to claim 4, wherein component (A) is a pyrroline type dye (A^1) of the formula (I) wherein R^1 is H, R^2 is C_4H_9 , and R^3 is 1-methyl-n-hexyl or is a mixture of the pyrroline-type dye (A^1) with a pyrroline-type dye (A^2) of the formula (I) wherein R^1 is H and each of R^2 and R^3 is C_4H_9 , which pyrroline-type dye mixture contains up to 10%, by weight of the total weight of the pyrroline-type dye mixture, of the dye (A^2).

30

6. A dye mixture according to claim 3, wherein component (A) is a pyrroline-type dye (A^3) or (A^4), each of the formula (I), or is a mixture of the dyes (A^3)

35

and (A⁴),

which dye (A³) is a dye wherein R¹ is H, R² is ethyl and R³ is n-octyl and

5 which dye (A⁴) is a dye wherein R¹ is H, R² is ethyl and R³ is 2-ethyl-n-hexyl.

7. A dye mixture according to claim 2, wherein D is a group of the formula (a), R² is as defined in claim 2 and R³ is C₁₋₆ alkyl.

10

8. A dye mixture according to claim 7, wherein R¹ is H or allyl, R² is 3-phenyl-n-propyl and R³ is C₄H₉.

9. A dye mixture according to any preceding claim,
15 wherein component (B) is at least one of the anthraquinone type dyes (B¹), (B²) and (B³), each of the formula (II) wherein Z_n is O and n is 2 or 3,

in which dye (B¹), R_B¹ is methyl

in which dye (B²), R_B¹ is methoxyethyl; and

20 in which dye (B³), R_B¹ is ethyl.

10. A dye mixture according to claim 9, which is a mixture of each of the dyes (B¹), (B²) and (B³).

25 11. A dye mixture according to claim 9, wherein component (B) is a mixture of the anthraquinone-type dyes (B¹) and (B²).

30 12. A dye mixture according to claim 11, wherein the ratio by weight of dye (B¹) : dye (B²) is from 30 : 70 to 60 : 40 inclusive.

13. A dye mixture according to claim 12, wherein the said ratio of dye (B¹) : (B²) is from 45 : 55 to 48 : 52.

35

14. A dye mixture according to any preceding claim, wherein the ratio by weight of component (A) : component (B) is from 3: 97 to 60 : 40 inclusive.
- 5 15. A dye mixture according to claim 14, wherein the said ratio of component (A) : component (B) is from 8: 92 to 35: 65 inclusive.
- 10 16. A dye mixture according to claim 1, wherein component (A) is a pyrroline-type dye of the formula (I), wherein R^1 is H, R^2 is C_4H_9 , and R^3 is 1-methyl-n-hexyl or a mixture thereof with up to 10% by weight of a pyrroline-type dye of the formula (I) wherein R^1 is H and each of R^2 and R^3 is C_4H_9 , and
- 15 component (B) is a mixture of anthraquinone-type dyes (B^1) and (B^2), given and defined in claim 9.
- 20 17. A dye mixture according to claim 16, wherein the ratio of component (A) : component (B) is from 10 : 90 to 30 : 70.
18. A dye mixture according to claim 17, wherein the said ratio is 6 : 33.
- 25 19. A dye mixture according to any one of claims 16 to 18, wherein the ratio, by weight, of dye (B^1) : (B^2) is from 45 : 55 to 48 : 52.
- 30 20.- A composition comprising a dye mixture according to any one of the preceding claims and at least one dispersing agent, surfactant or wetting agent.
- 35 21. A process for colouring a synthetic textile material or fibre blend thereof, which comprises applying thereto a dye mixture according to any one of

claims 1 to 19.

22. A process for colouring a synthetic textile material or fiber blend thereof, which comprises
5 applying thereto a composition according to claim 20, dispersed in an aqueous medium.

23. A process according to claim 21 or claim 22,
10 wherein the synthetic textile material or fiber blend thereof is a polyester or polyester-cellulose or polyester-wool blend.

15

20

25

30

35

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/GB 99/03300

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B67/22 D06P3/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 10248 A (ZENECA LTD ;CAVANAGH DENISE (GB); JAMES MARK ROBERT (GB); MEYRICK) 11 May 1994 (1994-05-11) cited in the application page 1, line 11 -page 3, line 10 page 10, line 30 -page 11, line 15	1-23
Y	EP 0 511 625 A (EASTMAN KODAK CO) 4 November 1992 (1992-11-04) abstract	1-23
Y	EP 0 591 736 A (BASF AG) 13 April 1994 (1994-04-13) abstract page 12, line 12 - line 28	1-23
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

21 December 1999

Date of mailing of the international search report

11/01/2000

Name and mailing address of the ISA
European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3018

Authorized officer

Dauksch, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/03300

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 198643 Derwent Publications Ltd., London, GB; Class A23, AN 1986-282768 XP002126339 & JP 61 207679 A (SUMITOMO CHEM IND KK), 16 September 1986 (1986-09-16) abstract & CHEMICAL ABSTRACTS, vol. 106, no. 16, 20 April 1987 (1987-04-20) Columbus, Ohio, US; abstract no. 121344f, abstract</p>	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Patent Application No

PCT/GB 99/03300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9410248 A	11-05-1994	AT 171466 T CN 1088233 A DE 69321249 D DE 69321249 T EP 0667887 A JP 8502776 T TR 28060 A US 5660598 A US 5865857 A	15-10-1998 22-06-1994 29-10-1998 28-01-1999 23-08-1995 26-03-1996 02-01-1996 26-08-1997 02-02-1999
EP 0511625 A	04-11-1992	US 5168094 A DE 69205323 D DE 69205323 T JP 2013927 C JP 5173017 A JP 7052244 B	01-12-1992 16-11-1995 23-05-1996 02-02-1996 13-07-1993 05-06-1995
EP 0591736 A	13-04-1994	DE 4232557 A CN 1090305 A JP 6240167 A US 5376150 A	31-03-1994 03-08-1994 30-08-1994 27-12-1994
JP 61207679 A	16-09-1986	NONE	